HANDBOOK

OF

TECHNICAL GAS-ANALY

BY

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SECOND ENGLISH EDITION.

Translated from the Third, greatly enlarged German Edition,
with some additions,

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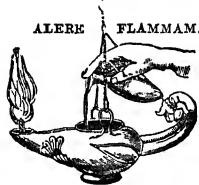
TRANSLATOR'S PREFACE TO THE FIRST EDITION.

EVERY one who has to make gas-analyses for technical purposes is aware that Professor CLEMENS WINKLER is the founder of technical gas-analysis as a distinct branch of analytical Chemistry. A few such processes were, of course, previously known and practised; but Winkler was the first to draw attention to the importance of this subject, to invent suitable apparatus, and to elaborate a complete system of qualitative and quantitative technical gas-analysis *, containing a vast number of new observations and methods, along with a very complete description of the work already done in the same direction by others.

The field first opened out by Winkler has been very successfully cultivated by other chemists ; and it is now quite usual, at any rate in Germany, to perform technical gas-analyses, not merely in chemical works, but for testing the efficiency of steam-boiler furnaces and such purposes. In England some of these processes have also been introduced ; but they are not as yet known and appreciated to the same extent as abroad. Hence it may not be unwelcome to English chemists to have a translation of a short treatise, just published by Winkler, which is primarily intended for *teaching* purposes—that is, for the use of teachers and students in public laboratories —but which likewise serves as a guide and a handy book to other chemists wishing to make themselves acquainted with the subject. This treatise is not intended, as was its predecessor, to furnish a complete enumeration of all apparatus hitherto proposed for technical gas-analysis, but merely to give representative examples of each kind of apparatus, embracing all the divisions of this branch of Chemistry. It may be confidently said that a person who has mastered the processes and apparatus described in this book will at once

* CL. WINKLER, ' Anleitung zur chemischen Untersuchung der Industrie-Gase,' Freiberg, 1877–79 (2 vols.).

comprehend and manage any other gas-analytical process or apparatus he may meet with or require for his special purpose. The scope of this book does not in any way embrace the methods of gas-analysis practised for purely scientific purposes, for instance, all those in which mercury is employed for confining the gases; but it will, for all that, have great interest for scientific chemists.

The selection which the Author has made from the large mass of material now accumulated was evidently, to a certain extent, dictated by special circumstances. German sources were mainly used by him, as these far more than sufficed for the purpose which he had in view—that of furnishing a sufficient number of illustrations for all parts of his field. The Translator has been under a strong temptation to supplement the book by some other examples of apparatus; but this proved unmanageable, as the present treatise would thus have lost its character, as indicated above, and as then, with greater pretensions, it might perhaps have been more open than it is at present to the objection that the treatment of the subject was not sufficiently exhaustive. The Translator has therefore contented himself with adding a few notes where they seemed to be specially called for, and with describing two apparatus of his own construction which have been found very useful just for industrial purposes, and which seemed to supply a want. All the additions he has made are marked, the text being in other respects a faithful rendering of the German original.

The Translator must acknowledge the most valuable services of Dr. Atkinson in looking over the proofs and improving the style of the translation.

All the apparatus mentioned in this book can be supplied by Messrs. Mawson and Swan, of Newcastle-upon-Tyne, or by any other dealers in chemical apparatus.

It is hoped, then, that English chemists, gas-managers, engineers, factory inspectors, and others interested in technical gas-analysis, will receive this work with favour, and that it will be as widely employed and as useful as Winkler's works have been in his own country.

Zurich, August 1885.

# TRANSLATOR'S PREFACE TO THE SECOND ENGLISH EDITION.

THE first edition of the German original of this book appeared in 1884, a second followed in 1892, and a third was published towards the end of 1901. In the meantime the first English edition became exhausted, so that a new issue would have been called for in any case. Professor Winkler kindly consented to allow the Translator to do his work from the proof-sheets of the third German edition, so that this present second English edition corresponds to the third edition of the original.

Although the scope of this work has remained primarily to furnish a help to the *teacher* and the *student* of technical gas-analysis, it has been greatly enlarged, as is proved by the fact that the number of pages has been increased by one-half. It does not even now purport to give a co
apparatus proposed for ᴛᴇᴄʜɴᴜᴋ
all the more important of these, including the valuable additions made to that part of technical analysis by Professor Hempel; and it will be found a sufficient guide and help in most cases to the practical and manufacturing chemist, as well as to the student. As before, only methods practically tried and approved by the Author have been recorded in this book.

The Translator has again introduced a few remarks of his own in the text, and has also made some additions describing his own apparatus more fully than is done in the original; but he has taken care to mark everything in such a way that the reader can never be uncertain as regards Professor Winkler's work and the portions added by the Translator.

Zurich, March 1902.

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INTRODUCTION.

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GENERAL REMARKS.

THE chemical examination of gaseous mixtures, for the purpose of quantitatively estimating their constituents, is usually effected by *measuring*, not by weighing, the latter, owing to the general physical behaviour of gases: gas-analysis being a volumetric process, and hence also called *gasometry*, or *gasometric* or *gasvo'umetric* analysis.

Consequently the results of gas-analyses are not usually expressed in per cent. by weight, but in *per cent. by volume.* In exceptional cases some of the gaseous constituents are estimated by weighing ; but, even then, the weight is reduced to the corresponding volume from the well-known weight of a litre of the gas in question.

Since the volumes of gases are essentially influenced by moisture, pressure, and temperature, they are measured when saturated with moisture and under the existing conditions of atmospheric pressure and temperature, as observed at the time by means of the barometer and thermometer. The volume found in this way (*uncorrected volume*) is afterwards *reduced to the normal volume ;* that is, from the volume actually observed it is calculated what volume the gas would occupy in a perfectly dry state at the normal barometric pressure of 760 millims. and at the normal temperature of 0° C. (*corrected* or *reduced volume*). This correction may be omitted if the analyses are very quickly performed or if they do not require any considerable degree of exactness.

The *analytical process* followed in the examination of gases generally consists in transforming one constituent after the other into a compound of a different state of aggregation. From the *contraction of volume* thus produced, the volume of the special constituent in question can be deduced directly or indirectly. This can be done :—

(1) *By direct absorption.*—For instance, carbon dioxide is taken up by a solution of potassium hydroxide, oxygen by moist phosphorus, carbon monoxide by cuprous chloride. They are thus dissolved out, which causes a decrease of the volume of gas originally employed to the extent of their own volume.

(2) *By combustion.*—Hydrogen is burned with oxygen, forming water. In this process two volumes of hydrogen unite with one volume of oxygen; both gases vanish as such, and a contraction takes place to the extent of three volumes. Hence the volume of the hydrogen originally present is found on multiplying by $\frac{2}{3}$ the contraction of volume observed.

(3) *By combustion and subsequent absorption of the products.*—Certain gases cannot be directly absorbed, nor are they transformed by combustion into compounds condensing of their own accord, but these compounds are capable of being absorbed. Thus methane is burned into water and gaseous carbon dioxide, which is absorbed by a solution of potassium hydroxide; 1 vol. of methane and 2 vols. of oxygen (altogether $= 3$ vols.) in this process yield 1 vol. of gaseous carbon dioxide. The contraction produced by absorbing the latter is $3 - 1 = 2$ vols. From this we see that the volume of the methane originally present in the gas can be found in three ways :—

(a) By dividing by 2 the contraction accompanying the combustion.

(b) By absorbing the carbon dioxide formed in combustion, whose volume is equal to that of the methane.

(c) By dividing by 3 the contraction of volume consequent upon the combustion and the absorption of the CO_2 formed.

Gaseous constituents which do not lose their gaseous state,

either by absorption or by combustion, or by combustion and absorption combined, are measured directly in the state of gas ; that is, they form the *residue* remaining at the close of the operation of gas-analysis. This case refers only to one gas, viz. nitrogen *.

In order to arrive at results which satisfy practical requirements, without laying claim to the utmost attainable degree of accuracy, *technical gas-analysis* must first and foremost aim at working by the simplest possible means and with the least possible waste of time. Scientific investigations are not tied to time and hour ; but where the question is that of practically controlling the working of some technical process, it is often necessary to get quickly an idea of this from time to time ; or it may be instantaneously wanted, even if that idea should be only a rough one. Analytical results, which the manager of the works can only receive from the chemist after the lapse of days or weeks, are in most cases entirely useless to him, let them be ever so accurate. This must be steadily borne in mind when working out methods of gas-analysis ; and, fortunately, the progress made during the last few years has shown that, although the procedure has been simplified, the accuracy of gas-analyses has steadily increased.

For measuring the gases we employ *measuring-vessels* of suitable construction, gauged and divided according to the metrical system, within which vessels the gases are confined. As *confining-liquid* we always employ pure water whenever practicable. Mercury should be avoided as far as possible ; glycerine and fatty oils, which do not offer the least advantage, but many inconveniences, must be entirely avoided. If gases very soluble in water have to be treated, they are either confined and measured between glass taps, avoiding any liquid ; or the soluble part of the gases is first estimated by absorbing it by means of a chemically active solvent of known strength, and only the unabsorbed gases are subjected to volumetric analyses. In such cases the absorbable gas is estimated by *titration*. In order to avoid any delay by unnecessary calculations, the strength of the standard solutions used for

* Argon and its congeners are never separated from nitrogen in technical analysis.—*Translator*.

made to correspond with the volume-weight
.s; so that a standard solution is considered
measure of it is capable of absorbing exactly
as in question, when corrected for pressure

·al estimation of gases is also sometimes per-
ises where one of the constituents of a gaseous
:˔ present only in small quantity, has to be
ipposes that the gas in question can be trans-
npound of constant composition, capable of

ion of the volume of a gas can take place :—

ct measuring ;
.ɪration ;
ɟ *weighing*.

osorption of gases is carried on either within the measuring-
us, or preferably outside the same in special absorbing-
. *Combustions of gases* are always made outside the mea-
suring-vessels. Combustions by explosion, whether with or
without addition of oxyhydrogen gas, should be avoided, if
possible. Care must be taken that during the analytical opera-
tions pressure and temperature suffer no essential changes; the
laboratory in particular and the confining and absorbing liquids
should have the same temperature; the influence of draughts,
radiant heat, and of other external agencies which alter the volume
of gases must be excluded from the apparatus.

CHAPTER I.

ON TAKING SAMPLES OF GASES.

SAMPLES of gases may be taken in various ways accordin̩
circumstances, but it is usually done by means of an aspir℩
Previously to collecting the gas, care must be taken to *remove*
air completely from the connecting-tubes and other intermedi␣␣
apparatus. This can be done by interposing in the connecting-
tube, immediately before its junction with the collecting·vessel, a
T-shaped branch whose lateral arm is joined to a small india-
rubber aspirating-pump (see below). By means of this pump it
is easy to remove the air between the place whence the sample
is taken and the collecting-vessel, and to fill the tubing with the
gas under examination; so that, on the commencement of sampling,
only the latter can get into the collecting-vessel. If the gas is
under pressure, so that it issues of its own accord, the employ-
ment of an aspirating-pump is evidently unnecessary.

1. *Aspirating-tubes.*

In order to take a sample of gas from any place, such as a
furnace, a flue, a chimney, &c., an *aspirating-tube* is introduced
into that place in the shape of a tube open at both ends, the outside
end being connected with the collecting-apparatus by means of an
india-rubber tube. It is of very little use to provide the aspirating-
tube with several branches, or with a slit as shown in fig. 1, with
the idea of getting a better *average sample* in this manner.
Although it is possible, by providing a movable cleaning-rod, to
prevent any soot or dust from stopping up the slit, still such a con-
trivance does not ensure a thoroughly trustworthy average sample,
because the rate of speed of a gaseous current passing through
a flue &c. is not the same throughout, and, owing to friction, is

considerably less in the neighbourhood of the walls. Moreover,
the gas is more quickly sucked in at that end of the slit which is

Fig. 1.
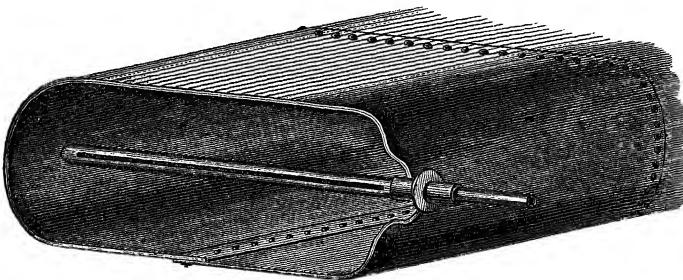
nearest to the aspirator.   Up to the present we do not know of
any process for taking from a moving current of gas such a sample
that it may be said to represent a perfectly correct average of
the whole bulk of the gas.   But it is possible to come very near
the truth by producing a strong *primary current* from the place

Fig. 2.
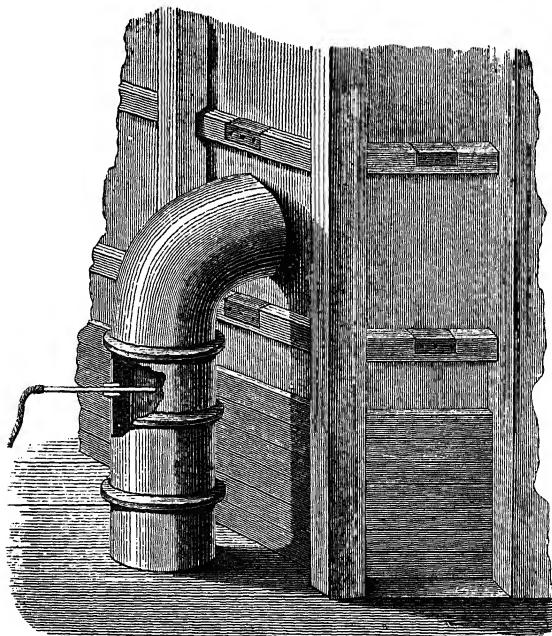
of sampling, and branching off a small *secondary current* from the former by means of a T-pipe, the latter current forming the average sample.

In cases where the composition of the gaseous mixture is subject to frequent and sudden variations (for instance, in furnace-gases, especially from periodically charged fire-places), it is preferable to refrain from collecting an average sample, and in the place of this to take a large number of special samples of the gas, each of which must be analysed separately.

The simplest and safest sampling can be performed with gases stored up in quantity, because these generally get mixed of their own accord by diffusion within the gas-holder *.

The selection of *the place from which the sample is taken* is sometimes a matter of importance. Thus, for instance, the efficiency of an apparatus for absorbing acid gases cannot be accurately ascertained, unless the samples of gas to be examined are taken *before entering the chimney* which forms the final part of the apparatus, since the gas may be diluted within the chimney by air entering from without.

The *material* of the aspirating-tube must be calculated to resist the prevailing temperature, and not to exert any chemical action upon the gas.

Wherever it is possible *glass tubes* are employed for this purpose, because they are easily constructed, inserted, and cleaned, and because they are neither acted upon by, nor do they act upon, the gases. If the temperature admits of it, the glass tube is simply fixed by means of a perforated cork or caoutchouc stopper, for instance in sampling the gases of pyrites-burners or vitriol-chambers (fig. 2). In such cases it is usually sufficient simply to bore a hole in the lead; but if greater durability and tightness are desired, a small piece of lead tubing may be soldered on to the hole.

A simple hole is also sufficient to admit of a cork and glass tube being introduced into the masonry of a chimney or flue. But it is preferable, especially where many samples of gas have to be taken at various times, to cement, once for all, a

* It should be observed, however, that this automatic mixture of gases by diffusion cannot be depended upon to take place expeditiously. Occasionally the various layers of gases within a large gas-holder show decided deviating composition for some time after filling the holder.—*Translator.*

porcelain socket-pipe into the hole made in the masonry by means of common clay or of fire-clay, and to tightly insert the cork with the glass tube into the socket.

Porcelain aspirating-tubes are employed, if the temperature of the place where the gas is to be sampled is high enough to soften glass. The porcelain tube should be of such a length that it projects a good deal beyond the outside of the masonry; in case of need the projecting part may be filled with a narrow-mesh wire-gauze, which usually suffices for cooling the gas passing through. If the gas is charged with soot or dust, the projecting part is filled with asbestos or glass-wool in order to retain the solid

Fig. 3.
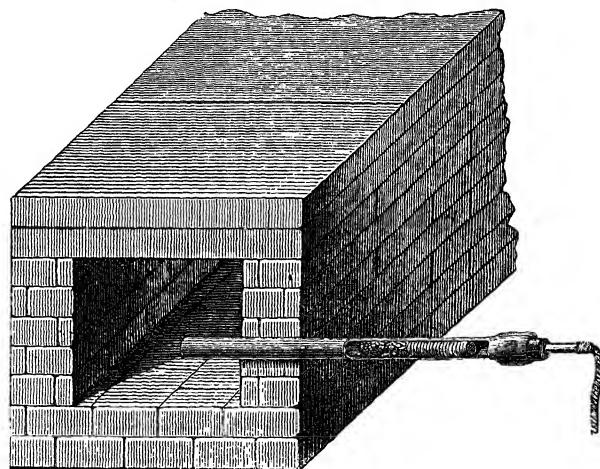
particles (fig. 3). Porcelain tubes should be gradually heated up, to prevent their cracking by the heat; unglazed earthenware pipes, which are sometimes employed instead, are certainly less sensitive to changes of temperature, but are not gas-tight, and on this account cannot be recommended.

Aspirating-tubes made of metal (iron, brass, copper, silver, platinum) have the advantage of not being fragile, and may be employed wherever the temperature is not high enough to cause the metal to fuse, or to allow the gases to diffuse, or to exert a chemical action upon them. But an inconvenient property of metals is their great conductivity of heat. Corks inserted into them may be charred; india-rubber tubes, joined to them, generally

stick fast and soften, or melt altogether. Nevertheless metallic aspirating-tubes cannot be dispensed with in many cases, and it may hence become necessary, to avoid the drawbacks just mentioned, to provide them with cold-water jackets. In order to cool the whole length of tubing, the following system may be adopted :—

Three copper tubes of different width, the metal of a thickness of 1 or 2 millims., are connected in the way shown in fig. 4. The innermost tube a is 5 millims. wide, and forms the aspirating-tube proper; it is surrounded by the second tube b, 12 millims. wide, which is soldered up tight at one end, the other end towards A being left open. This tube has a side-branch d, provided with

Fig. 4.
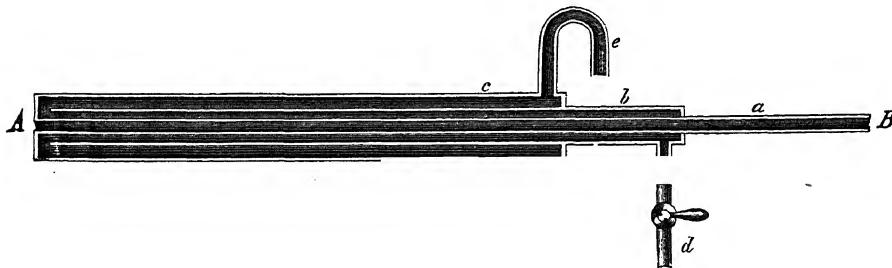
a stopcock, for admitting the cooling water. The outer jacket is formed by the tube c, 20 millims. wide, which at the end A is soldered to the tube a, at the end near B to the tube b. The tube c is also provided with a branch e, through which the cooling water, which has been heated on its way through the tubes b and c, is run off again. The length of the tube AB may vary according to circumstances; usually 0·6 to 0·7 metre (about 2 feet) will suffice. The inlet and outlet for the cooling water should be made wide enough to admit of a rapid flow of water, and so prevent any formation of steam.

In order to employ this apparatus for withdrawing gases from a heated furnace, a hole is made in a suitable place in the furnace-wall, about 3 centims. (say $1\frac{1}{4}$ inch) wide. The stopcock d is connected by an india-rubber tube with a water-pipe; it is then opened, and, as soon as the water issues at e, the end A is introduced through the hole into the furnace. The joint is at once made tight by a wet mixture of fire-clay and common clay. The end a is now connected with the reservoir for the gas and the

aspirator, in order to withdraw a sample of the gas.   Water should be caused to flow rapidly through the tubes up to the moment the apparatus is taken out of the furnace.

A similar, but simplified combination of pipes has been recommended by Drehschmidt (fig. 5).   The aspirating-tube a, 4 or 5 millims. wide, is surrounded by a jacket b, closed at both

Fig. 5.
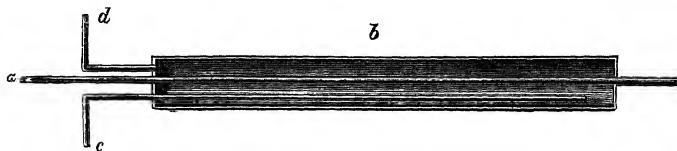
ends, into which cold water is introduced by the supply-pipe c, running away continuously at d and thus cooling the inner pipe. The whole is made of copper and the joints are brazed.

Very hot gases should be sucked off slowly and with careful cooling, because their constituents may be in a state of *dissociation*. When examining gaseous mixtures, whose dissociation has partially become permanent in consequence of violent cooling, very erroneous conclusions may be arrived at; in such cases especially we may expect to find carbon monoxide coexisting with oxygen.

It has also been attempted to cool the gases by immediate contact with water, in the manner shown in fig. 6.   The copper tube, 6 to 8 millims. wide, is U-shaped. The part E C, which is intro-

Fig. 6.

duced into the hot gas, is provided with a number of fine cuts, 0, 0' 0'', 0''', made by a saw, for admitting the gas. m n is a copper disk, by which the tube is fastened to the outside of the wall of the furnace.   In order to start the apparatus the stopcock A is opened, and water is thereby admitted, which runs through the bent tube A C B, and is carried off by an india-rubber tube into
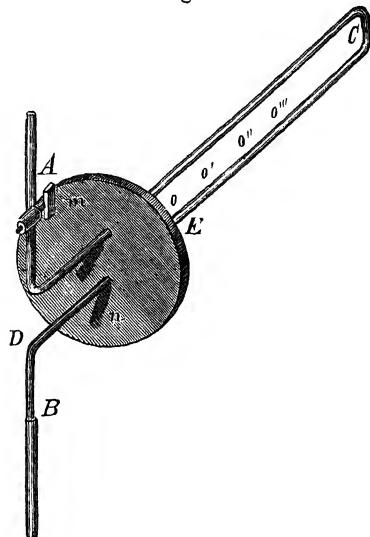
a gas-holder filled with water, where the water and the gas carried away with it are separated. At first a little water squirts out through the saw-cuts, but soon the tube $C\ D\ B$ begins to act as a siphon, and, if the cock A is set rightly, gas is aspirated through the saw-cuts and collected in the gas-holder.

As in this process the gas is brought into intimate contact with a large quantity of water, it cannot be avoided that certain gases, e. g. carbon dioxide, are absorbed to a considerable extent. Hence this manner of sampling can only be employed in a restricted number of cases ; but it may do good service where it is only a question of finding the relative proportions of gases possessing a slight solubility in water, such as oxygen and nitrogen.

2. *Aspirating Apparatus.*

In the last-mentioned case the conducting-tube forms at the same time the aspirator, but usually a special aspirating apparatus is employed in taking samples of gases, that is, special apparatus, as for

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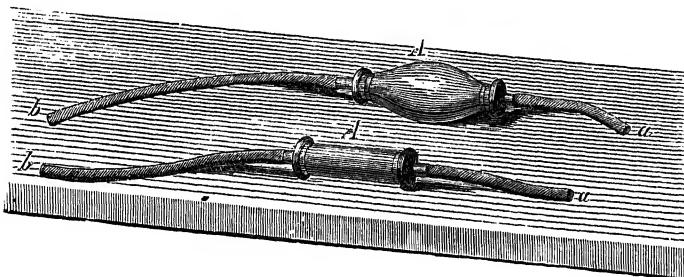
instance, *india-rubber aspirating- and force-pumps (hand or foot blowers)* of simple construction, as met with in commerce in various sizes (fig. 7). They consist of a stout vessel A, with cylindrical ends, which are stopped up with turned and perforated wooden bungs, provided inside with a very simple kind of valve (viz., leather clacks with a pasteboard strengthening). India-rubber tubes of differing length are attached to these bungs ; the shorter piece a, about 20 centims. long, forms the aspirating-tube, the longer piece b, about 40 centims. long, the discharging-tube. On compressing the vessel A by hand or by foot, its gaseous contents are forced out through b ; when the pressure is relaxed the elastic

vessel resumes its former shape, and is thereby filled with a new supply of gas through *a*. By a continued alternation of these two manipulations considerable quantities of gas may be aspirated and forced away within a short time, say 12 to 18 litres per minute, and the valves close tightly enough to overcome a pressure of several metres of water. This contrivance is extremely convenient for filling a bottle, a tube, or any vessel whatsoever with the gas to be examined. In this case no confining (luting) liquid is required, but there must be an ample supply of the gas in question, for the air previously present can only be assumed as having been entirely replaced by the gas provided the five-fold volume of the latter has passed through the blower.

Where high-pressure steam can be had, gases may be aspirated continually or for a great length of time by means of a *steam-jet aspirator* (fig. 8). A strong glass tube, about 3 centims. wide, or

Fig. 8.
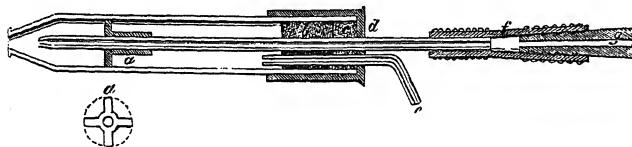
in lieu of this a metallic tube of a length of 20 to 25 centims., is drawn out at one end to an orifice of 6 millims. width ; a steam-pipe is fixed in its longitudinal axis in such a way that its point, tapering to 2 millims. bore, ends about 12 millims. behind the orifice of the outer tube. Near this point the steam-pipe is kept in its place by a ferrule *a*, made of wood or metal ; at the other end it is tightly fixed in the cork *b*, which, in its second perforation, carries the tube *e*, through which the gas is aspirated. This cork, to make the juncture firmer, is covered with a layer of cement *c*, and the whole is confined in a metal ferrule *d*. The aspirator should be joined to the steam-pipe *g* by an india-rubber tube with hemp lining *f*, since ordinary india-rubber tubing does not resist steam-pressure.

Apart from these "dry" aspirators, a considerable number are constructed with a water-luting.

It is frequently necessary to aspirate a gas continuously for a long time, whether in order to measure its volume in a gas-meter, or to take a smaller sample from it, or to absorb one of its

constituents present in very small quantity. In such cases it is customary to apply that kind of aspirator in which the gas is carried away by a jet of water, and whose efficiency may be sufficient to overcome the atmospheric pressure. Very many such apparatus have been constructed, of which only a few of the best are here described.

Bunsen's water-air pump * (fig. 9) consists essentially of a cylindrical glass vessel *A*, into whose contracted upper end a narrower glass tube is soldered, communicating on one side with the glass vessel *B*, and on the other side reaching nearly down to the lower contraction of *A*, where it ends in a fine orifice. To the lower end of *A* is joined a lead pipe *b*, 8 mm. 10 to 12 metres long, and bent up at the lower end so that some water is retained here. The side-branch *a* is connected with a water-reservoir or with the service-pipe ; the flow of water, which need not take place under pressure, can be once for all set to a certain rate by means of a screw-clamp, and completely shut off by another. If water is run in through *a*, the lead pipe

Fig. 9.

b is filled with a column of water balancing the weight of the atmosphere, and the jet of water following this carries air along through *c*, in order to yield it up only at the lower end of the lead pipe. If *c* remains open, the air is continuously and strongly sucked in, so long as the flow of water is not interrupted. If, however, *c*, or a space communicating with *c*, is closed, a vacuum is produced, corresponding to the Toricellian vacuum of the water-barometer formed by the apparatus. The vessel *B* is not essential for the purpose of aspiration ; its object is principally to retain any liquid carried along mechanically, and to admit of discharging the latter through
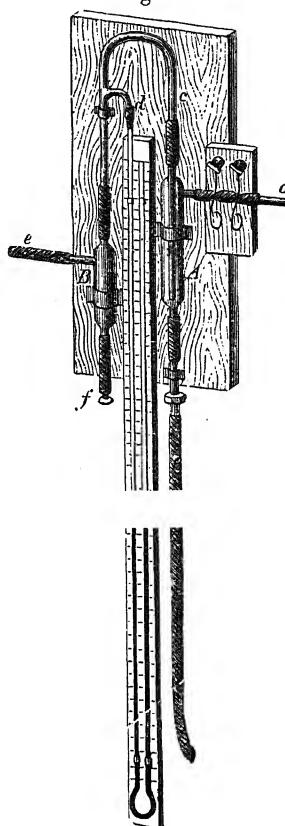
* Really invented by H. Sprengel.—*Translator.*

f from time to time. The tube *d* is connected with a mercurial pressure-gauge, which indicates the progress of the evacuation ; *e* is the continuation of the aspirating-tube *c,* and is connected with the space which is to be evacuated, or from which a sample of gas is to be taken. Bunsen's pump requires no head of water, but a considerable length of downward pipe as above-mentioned ; if, however, the purpose is not that of complete evacuation, but merely of aspirating gases, the downward tube may be shortened down to 1 metre, or even less than that. The long lead tube *b* may then be replaced by an india-rubber tube, closed at the lower end by a bent glass tube.

The *water-jet pumps* as constructed by Arzberger and Zulkowsky, H. Fischer, Körting Brothers, Th. Schorer, and others work well and do not require any height of fall for the waste water ; but, on the other hand, they require a head of 5 to 10 metres of water for feeding. Their construction, which has been very

Fig. 10.
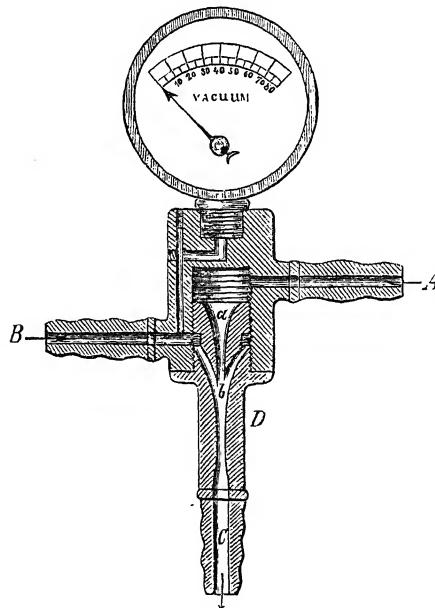
much varied, is apparent from fig. 10. The water enters at *A,* issues from the conical tube *a,* 1 millim. bore, carries along the air entering through *B,* passes the contracted part *b,* and runs

off at *C*. The three tube-ends *A, B,* and *C* are connected with
the corresponding pipes by elastic tubing ; the neck *D* is held
in a support. A small vacuum-meter communicating with *B*
indicates the degree of lessened pressure.

Of a simpler kind but hardly less efficient are the various *water-
jet pumps made of glass,* which are found in commerce. These can
be connected with any water-tap by means of thick india-rubber
tubing ; they are easily moved about and are, moreover, deep. To
these belong *Finkener's aspirator* (fig. 11), where the water enters

Fig. 11.   Fig. 12.
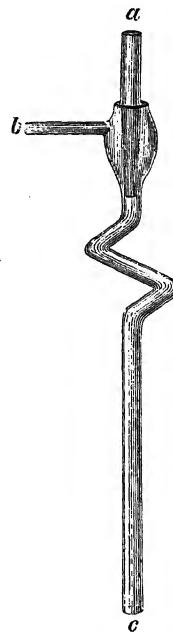
from the service-pipe through the tube *a,* which is drawn out to a
point ; runs through the tube *c,* which is bell-shaped at the top,
contracted in the middle, and again widened at the bottom end ;
and aspirates air through *b,* which forms a frothy mixture with the
water issuing at *c.* In order to diminish the fragility of the
apparatus, it is usual to make the lower, tapering tube separate
and connect it with the upper part by an elastic joint. Very
efficient also are *Geissler's aspirating-tubes,* which can be understood
from fig. 12 without special explanation.

Another kind of apparatus admits of both aspirating and collecting the gases, sometimes also of measuring them, or rather that part which is not sensibly soluble in water. In many cases the analytical apparatus itself, such as the *gas-burette* or the gauged *collecting-bottle*, is employed as an aspirator, by being filled with water, which is made either to run off within the space containing

Fig. 13.
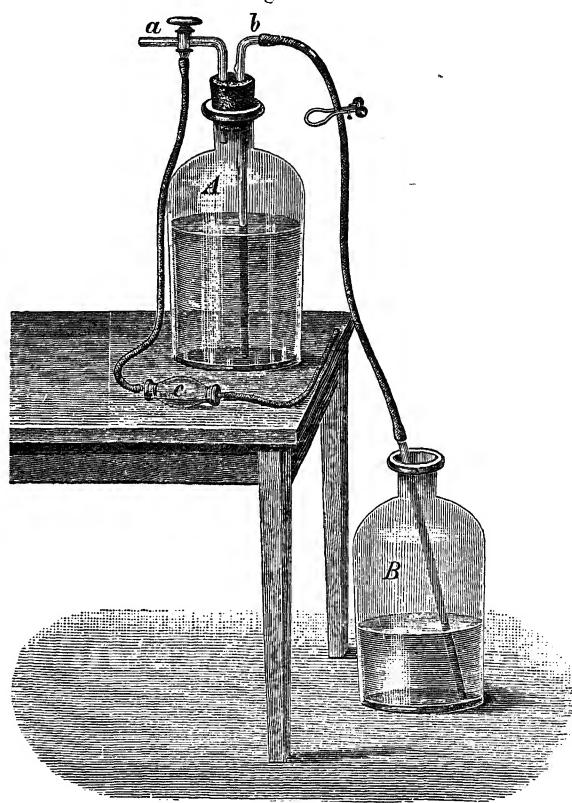
the gas to be examined or after connecting the apparatus with the aspirating-tube.

If somewhat large quantities of gases have to be collected, an *aspirating-bottle*, as represented in fig. 13, may be employed. This bottle *A* is placed on a wooden stool; its india-rubber cork is provided with a glass stopcock *a* and a tube *b*, reaching nearly down to the bottom, and on the outside is connected by means of an elastic tube with a straight glass tube of sufficient length to act

as a siphon, capable
bottle. The connect
clamp, which also p
regulated. Before ta
with water by so alte
that no air-bubbles re
top of the stopcock a
is removed from the
the three-way tap ; th
aspirated by allowing
ment can, for instar
sample is to be taken
the whole course of
reduced current shot
collected in bottle *A*.

Robert Muencke's d
especially where volum
proximately equal have
to be aspirated. T
cast-iron pillars support in suitable
bearings a steel spindle, to which
are attached, in opposite directions,
two cylindrical glass vessels of
known volume, communicating by
means of a stopcock, which also
regulates the outflow. A simple
spring arrangement, attached to
the front part of the spindle or
the upper part of the front pillar,
serves for fixing the glass vessels
in a perpendicular position. Each
glass cylinder is closed with a brass
plate affixed with screws, pierced by
a bent brass tube reaching nearly
down to the bottom of the vessel,
and on the outside connected with
an elbow-piece, to which the two pieces of tubing are attached
which communicate with the stopcock fixed to the ground plate.
This stopcock is marked for the vessels *A* and *B*, and is bored in
such a way that, if turned as in the figure, it brings the upper
vessel *A* into communication with the apparatus through which gas
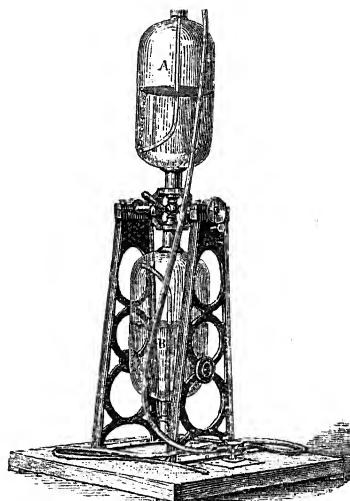
is to be aspirated, and at the same time connects the lower vessel *B* with the atmosphere.   When the upper vessel is run off, the button of the spring-arrangement is pressed, the cylinders shifted round the spindle by 180°, and the lower stopcock turned to the same extent. In this position the vessel *B* is connected with the gas-apparatus and *A* with the atmosphere. Thus this double aspirator per- mits of almost continuous action without any change of tubing.

Fig. 15.

A very convenient form of *zinc aspirators* is shown in fig. 15. The vessel *A*, con- taining 10 to 15 litres, is placed in a wooden stand ; it ends at the top in a stopcock *b*, and at the bottom in a slightly tapering tube, provided with the tap *c*, and bearing a thin brass tube *d*, through which the water can flow off regularly without air- bubbles entering the vessel. The side-branch *a*, also provided with a tap, serves for filling with water.   The aspirator should be filled with water of the same temperature as the laboratory ; or, if the water is taken from a service-pipe, it must be allowed sufficient time to acquire that temperature. This is indispens- able if the aspirator is to serve at the same time for measuring the volume aspirated, for which purpose it is very well adapted. When employing it for such measurements, the tap *b* is con- nected by means of an air-tight screw-socket with a glass T- piece, the upper limb of which ends in a small mercurial pressure- gauge, whilst the side limb is connected with the aspirating-pipe. By opening the taps *b* and *c* the gas is aspirated and the water
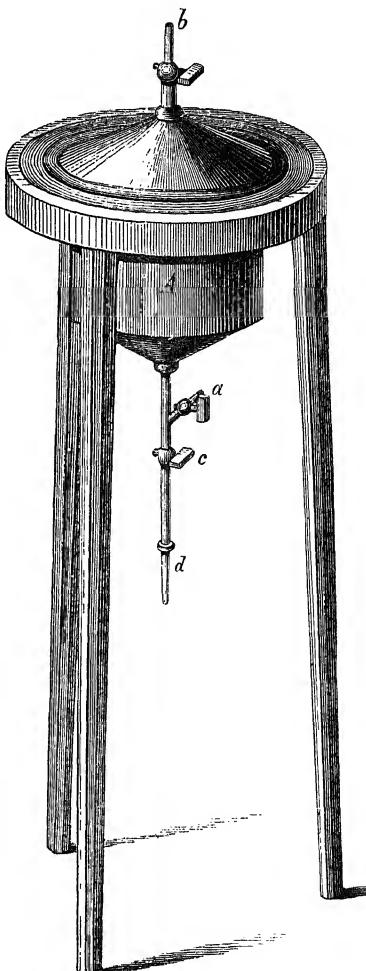
which runs off is collected in a litre-flask placed below. The moment the water in the latter has reached the mark, the tap *c* is closed, but *b* is only closed the moment the pressure-gauge has come to the level again. When this happens a volume of gas exactly equal to that of the water run off has been aspirated.

For aspirating and at the same time measuring large volumes of gas, the *automatic aspirator of J. Bonny* * can be employed. The essential feature of this apparatus (fig. 16) is a metal vessel *A*,

Fig. 16.
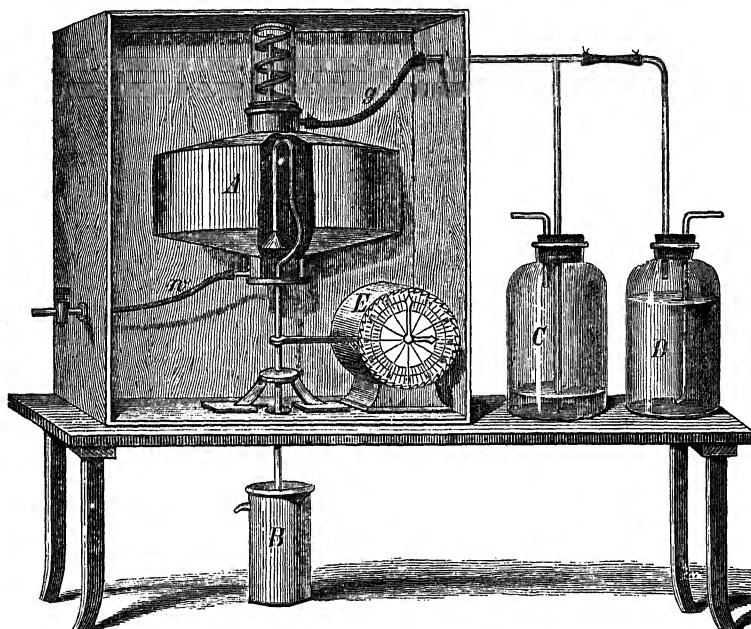
containing on the inside a siphon whose shorter funnel-shaped limb reaches down to the lower part of the vessel, whilst the longer limb is carried through its bottom and dips into the vessel *B*, in which is water at a constant level. Through the india-rubber tube *w*, connected with the water-service, the vessel *A* can be filled with water. The tube *g* serves for the entrance and exit of the gas; it communicates with the bottles *C* and *D*, the first of which serves as a water-lute, the second

* Sold by Cornelius Heinz & Co., Aachen: price 75 marks.

for containing the absorbing liquid through which the aspirated gas is to be passed. The apparatus begins to work as soon as the tap of the service-pipe is opened and water enters into A. Whilst this vessel is filling the gas contained in it escapes through the bottle C; but as soon as the water-level is up to the bend of the siphon, this begins to act and the water flows into the vessel B. If the supply of water through w is regulated so that it is less than the outflow into B, the level of water in A must sink, and the gas will be aspirated through the absorbing-bottle D, from which it passes into A. But as soon as the water has run off to the end of the shorter limb of the siphon, the latter ceases to act, and only starts working again when the vessel A has been again filled with the water which continuously flows through w. The volume of gas aspirated every time the siphon acts is equal to the contents of the vessel A between the highest and lowest levels, which has been gauged once for all : the number of times is registered by the indicator E, which moves every time the vessel A is raised. The latter is hung from the top of a portable box by means of a spiral spring, which is compressed when A is filled and extended as A empties. This contrivance causes the differences of level between A and B to be equalized.

3. *Vessels for collecting, keeping, and carrying Samples of Gases.*

Unless unavoidable, a sample of gas should not in any case be kept for any length of time, but ought to be transferred at once to the analytical apparatus—such, for instance, as a gas-burette or an absorption-bottle—in order to be instantly analyzed. A rule to be observed in cases where it is unavoidable to employ water-luting is this: to bring the water merely into superficial and momentary contact with the gas, but *never to pass the gas through the water itself*, as is done in a pneumatic trough. Otherwise the solvent action of the water, which is entirely different towards different gaseous substances, would unavoidably alter the composition of the gas to a sensible extent.

If, however, the collection of the gas in a separate vessel for the purpose of keeping it for some time or transporting it to some distance cannot be avoided, care must be taken not merely to exclude the air completely from it, but also to entirely remove the water employed in taking the sample, as this would otherwise

exercise a solvent action upon some of the constituents of the gas. This holds good for all cases in which the collecting-vessel itself is used as an aspirator, by filling it with water and causing the gas to be aspirated by the outflow of the water. If the sampling takes place without contact with water, by pumping the gas by means of an india-rubber pump into the dry collecting-vessel or by aspirating it through the same by means of an aspirator, this must be continued long enough to ensure the complete expulsion of all air.

India-rubber collecting-vessels should, as a rule, be avoided, because many gases are diffused through their walls, even if thick or impregnated with grease. This is the case to a very considerable extent with sulphur dioxide and hydrogen; whilst, for instance, mixtures of oxygen, nitrogen, carbon dioxide, and carbon monoxide (that is, the gases produced by combustion of fuel) can be kept unchanged in such vessels for several hours, but never till the next day.

Glass collecting-vessels, which are usually employed in the shape of tubes, are only absolutely and permanently tight provided they terminate in capillary ends which are sealed by the lamp after introducing the gas. If the enclosed gas is afterwards to be transferred to a gas-burette, narrow india-rubber tubes are attached to both ends; these are filled with water and closed by means of glass rods or pinch-cocks, after which the sealed ends may be broken within the india-rubber tubes by external pressure. In most cases, however, it is sufficient to close such collecting-tubes from the outset with india-rubber stoppers, or tubes stopped by means of glass rods or pinch-cocks (figs. 17 and 18).

In this case the end of the tube, provided with the india-rubber tube, is connected with the gas-burette, previously filled with water; the other end is made to dip into a vessel also filled with water; the cork &c. is opened below the water, and the water contained in the burette is run off till the gas has been carried into the burette, water taking its place in the collecting-tube.

Zinc collecting-vessels are especially employed for containing and transporting larger volumes of gases; and they have been found to answer very well in all cases in which the metal does not act upon the gas. The best form is that shown in fig. 19. The vessel is 50 centimetres long, or 60 centimetres including the conical ends, and has a diameter of 16 centimetres, so that it holds 10 litres of gas. Both ends have necks of 15 millimetres width, which

can be tightly closed by soft india-rubber corks or by the well-known porcelain knobs with india-rubber padding, which are pressed down by a hinge and lever. The vessel is hung from three thin brass chains, fitted at the top in a ring, and can thus be conveniently carried by hand, even when filled with water, in order to take a sample of gas in the proper place. If the outflow is to be slow or capable of being regulated, the solid corks are replaced

Fig. 19.
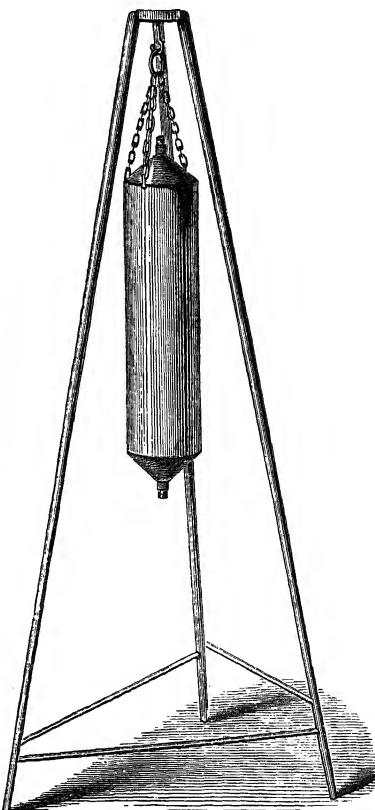
Fig. 18.

Fig. 17.

by others fitted with glass tubes and provided with screw pinch-cocks. Such vessels are employed in large numbers for taking samples of pit gases in the Saxon coal-pits, and sending them for analysis to the laboratory of the Freiberg Mining Academy.

CHAPTER II.

ON THE MEASUREMENT OF GASES.

General Remarks. Corrections.

THE volume of a gas can be found directly or indirectly. It is estimated, either

> 1st, volumetrically ;
> 2nd, by titration ; or
> 3rd, gravimetrically.

The quantity found is in all cases expressed in *per cen. volume.*

Every gas has the tendency to expand and fill any space offered to it ; it possesses a definite *expanding power*, which, in the state of rest, is exerted as a permanent pressure, the amount of which is called the *tension* or elastic force of the gas. All gases under the same (ordinary) circumstances possess the same tension ; they all are subjected to the same law as to their expansion and contraction.

The tension, and therewith the volume, of gases depends upon—

> 1st, the pressure ;
> 2nd, the temperature ;
> 3rd, the state of moisture.

We measure gases in their condition at the time at which the measurement is made—that is, at the atmospheric pressure as indicated by the barometer and at the temperature as indicated by the thermometer; and finally, since we work with water as the confining liquid, always in a state of complete saturation with moisture. Hence the conditions under which gases are measured may be very different, and may vary during the analysis even from one

observation to another. Every such change, unless duly taken into account, might cause very considerable errors. Hence it is indispensable, in many cases, to make *a correction*, consisting in reducing the volume of gas, which is observed in varying but known conditions, to that volume which it would possess at the normal barometric pressure of 760 millimetres, at the normal temperature of 0° C., and in the dry state. By general consent this is regarded as the *normal state of a gas.*

The reduction of the volume of a gas to the normal state is made by aid of a formula derived from the following observations :—

1. *Pressure.*—According to Boyle's law, the volume of a gas is in inverse ratio to the pressure upon it. Hence, if

$V_0 =$ the volume at normal pressure sought,

$V =$ the volume at the barometric pressure B,

$B =$ the state of the barometer at the time of the observation,

we shall have

$$V_0 = \frac{VB}{760}.$$

2. *Temperature.*—The expansion by heat of a gas is $\frac{1}{273}$ of its volume at 0° for each degree Centigrade.

Hence, if a gas measures 273 cub. centims. at 0°, it will measure $273+1$ cub. centims. at 1°, and at $t°$ $273+t$ cub. centims. If, therefore,

$V_0 =$ the volume of the gas at the normal temperature,

$V =$ the volume of the gas at the temperature t,

$t =$ the degree of temperature at the time of observation,

we shall have

$$V_0 = V \frac{273}{273+t} \quad \text{or} \quad \frac{V \times 273}{273+t}.$$

3. *State of Moisture.*—When a gas is saturated with moisture by contact with water, it always takes up the same quantity of water in the same conditions. This water is itself transformed into the gaseous state ; it therefore exerts a certain pressure, and this pressure, *the tension of aqueous vapour,* increases with the temperature, owing to the increased formation and expansion of that vapour. That tension, expressed in millimetres of mercurial pressure f, has been determined experimentally (compare Appendix), and must be deducted from the observed barometric pressure $(B - f)$.

From the preceding considerations we deduce the following *formula, which embraces all corrections* :—

$$V_0 = \frac{V \times 273 \times (B-f)}{(273+t) \times 760}.$$

Suppose a gas, saturated with moisture, to occupy a volume of 1000 cub. centims. at 738 millims. barometric pressure and 20° C. ; its volume in the dry state, at normal pressure and temperature, will be

$$\frac{1000 \times 273 \times (738 - 17\cdot4)}{(273+20) \times 760} = 884\cdot4 \text{ cub. centims.}$$

The reduction of the volumes of gases to the normal state may be omitted in analytical estimations which are rapidly performed, as material changes of pressure and temperature are not then to be expected ; so also in cases in which only approximately correct results are required.

When a gas is estimated by titration or by gavimetric analysis, its volume is found at once in the corrected state. If one of the gaseous constituents has been estimated, say, by titration, and another volumetrically, it may be desirable to calculate the former for the volume which it would occupy at the then existing barometric pressure and temperature, and in a state of saturation with moisture.

The following formula serves for *reducing the volume of a gas from the normal state to that which it would occupy at a different barometric pressure and temperature, and in a state of complete saturation with moisture* :—

If V = the volume of the gas at the barometric pressure B and the temperature t, saturated with moisture,

V_0 = the volume at 760 millims. pressure, at 0° C., and in the dry state,

we have

$$V = \frac{V_0(273+t)760}{273(B-f)}.$$

The *observation of the atmospheric pressure* is best made by means of *Bunsen's siphon barometer* (fig. 20), which is provided with a millimetre-scale etched on each of its limbs, and is held in a vertical position by the aid of a stand. The reading is made with the telescope of a cathetometer (fig. 21), which is

placed at a distance of 2 or 3 metres. The sum of the readings on both limbs indicates the barometric pressure. In certain cases it is sufficient to employ a small aneroid barometer.

Fig. 20.
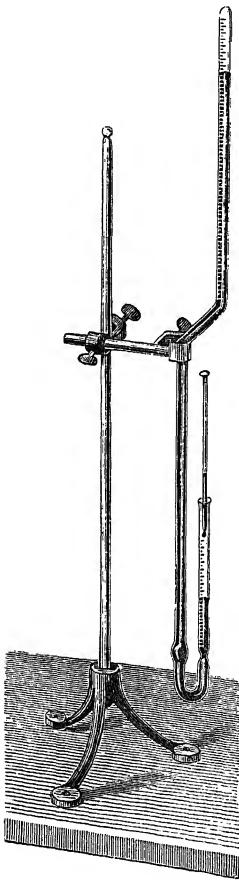
Fig. 21.
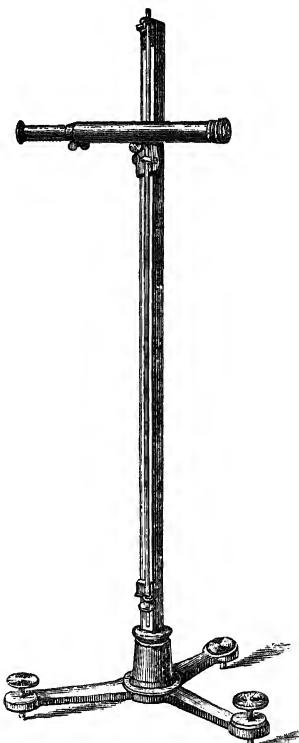
The *temperature* is observed by means of a small thermometer, divided into tenths of a degree, which is loosely placed in the shorter limb of the barometer.

An apparatus for the expeditious reduction of the volumes of gases to the normal state without the necessity of observing the thermometer and barometer was first proposed by U. Kreusler

(Ber. der deutsch. chem. Ges. 1884, xvii. p. 29) and afterwards constructed in a more convenient shape simultaneously by the author (Cl. Winkler, ibid. 1885, xviii. p. 2533) and the translator (G. Lunge, Chemische Industrie, 1885, p. 163). It is shown in fig. 22.

An iron stand with two arms carries two perpendicular glass tubes, connected at the bottom by a thick india-rubber tube ; one of these is the measuring-tube, the other the level-tube. The measuring-tube, *A*, is enlarged into a bulb at the top and is closed by a small, slightly greased, and absolutely tight glass tap *. It holds exactly 100 c.c. from the tap to the zero mark ; the division marked on the cylindrical part extends from the zero point to 5 c.c. upwards and 25 c.c. below, so that from 95 to 125 c.c. can be read off accurately to 0·1 c.c. These two extreme values would correspond to 100 c.c. air under normal conditions, saturated with moisture, when brought to 800 mm. B and $0°\,t$ on the one side, or to 700 mm. B and $30°\,t$ on the other side, and thus embrace all values occurring under ordinary circumstances. Tube *A* is held vertically in the lower arm of the stand, the division being completely in view.

The level-tube *B* is open at the top, which is protected by a dust-cover. It is held in the lower arm of the stand and can be moved up or down by means of a screw-clamp. It need not hold more than 30 c.c.

In order to set the apparatus once for all for permanent use, a

Fig. 22.

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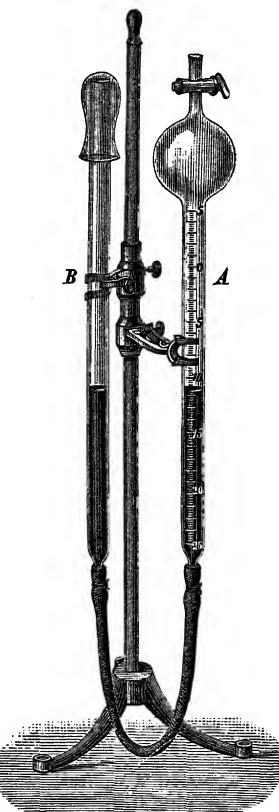
* Experience has shown that no ordinary tap holds tight in the long run the means of attaining this end will be discussed later on, when describing the gas-volumeter.—*Translator*.

few drops of water* are introduced into tube *A*, an approximately sufficient quantity of mercury is poured in, the whole is placed in a cool room, together with a barometer and thermometer, and after a few hours, or better the next day, the state of both the barometer and thermometer is accurately ascertained. According to the formula :

$$V = \frac{100 \times (270 + t) \times 760}{273 \times (B - f)},$$

it is calculated what volume 100 c.c. of air, assumed to be in the normal state, would occupy under the actually existing conditions. The tap being left open, the level-tube is raised or lowered to the point where the mercury level indicates precisely the calculated volume, and the tap is now closed. The volume of air thus confined increases or decreases with every external change of pressure and temperature exactly in the same ratio as another gaseous volume, present in the same room and intended to be measured, so that the normal volume of the latter can be calculated by simple proportion, after having brought the mercury in both limbs of the apparatus to the same level and read off the volume indicated on tube A. For if we call

V the observed volume of air in the tube at the ruling baro-
    metric pressure and temperature,

V_0 the same in the normal state (constantly $= 100$),

V^1 the volume of the gas to be examined at the ruling pressure
    and temperature,

V_0^1 the same in the normal state,

we have the proportion :

$$V : V_0 = V^1 : V_0^1.$$

Compare later on the mechanical reduction by Lunge's gas-volumeter.

G. Lunge has also modified this instrument so as to yield the reduced volume by a simple multiplying operation, and he has described the preparation of such reduction-tubes in a fit state for

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* In those cases where the gas to be measured is sure to be in the dry state, *e. g.* the nitric oxide given off in the analysis of nitrous and nitric compounds by means of the nitrometer, the reduction instrument may be adapted to this special use by putting in a drop of concentrated sulphuric acid, in lieu of water, and calculating accordingly.—*Translator.*

carriage to a distance (Chem. Zeit. 1888, p. 821 ; Zeitsch. f. angew. Chemie, 1890, p. 227) *.

Another correction apparatus is the *Gas-baroscope*, constructed by J. Bodländer, on the principle of gravimetrically estimating the gas (Zeitsch. f. angew. Chemie, 1894, p. 425).

An *approximate correction*, for cases where no great accuracy is required, can be at once made by ascertaining the difference between the volume of a gas in the normal state and that which it possesses under average *local* conditions of pressure and temperature. Thus the yearly average of barometric pressure at Freiberg is 725·6 mm., the mean temperature is 7°·0. 1 c.c. of gas in the normal state, if saturated with moisture, would under these average conditions occupy 1·085 c.c., and an approximate correction would be effected by dividing the read-off volume of gas by the above figure. But we must consider that the temperature of the laboratory is usually above the annual mean, and it is preferable to make the calculation accordingly. Allowing a mean pressure of 725·6 mm. and a temperature of 20°, the correction factor would be 1·135. The real average of observations made in the Freiberg laboratory corresponds to the factor 1·118 †.

I. Direct Volumetrical Estimation.

A. *Measuring in Gas-burettes* (Nitrometer, Ureometer, Gas-volumeters).

For measuring small volumes of gases, from 0·1 to 100 c.c., we employ *gas-burettes* of various construction. These are cylindrical glass tubes, usually graduated in cubic centimetres, which can be closed at the top and bottom by glass cocks or pinch-cocks, or hydraulically sealed, and whose division begins or ends at the upper tap. When the graduation is not required to extend the entire length of the tube, the upper portion is usually enlarged into a bulb or a wider cylinder, in order to shorten the tube, which may be useful for practical purposes.

It is unnecessary to say that gas-burettes, as well as all other apparatus serving for gas-analysis, must be correctly gauged and

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* These modifications, as well as the original instrument, have become obsolete by the construction of the gas-volumeter.— *Translator*.

† It is evident that errors up to 10 per cent. may be caused by this method, which consequently can serve only for very rough approximations.— *Translator*.